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DETERMINATION OF HEAT OF COMBUSTION OF SOLID WASTES FROM ULTIMATE ANALYSIS

A Solid Waste Research
Open-File Report (RS-03-68-17)
written by
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(Restricted Distribution)
submitted to
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ABSTRACT

The Dulong formula which determines heat of combustion (British thermal units per pound, Btu/#) of coal from an ultimate analysis is not applicable for solid wastes samples. However, with modifications and additions the formula can reasonably estimate heat of combustion of solid waste samples. This paper discusses these modifications and additions to the Dulong formula.

INTRODUCTION

The heat contents and ultimate analyses of the solid waste materials to be incinerated are necessary to determine the efficiency of incinerators and to successfully design future incinerators. Efficiency of an incinerator is calculated by establishing energy and material balances between the flow of materials in and out of the incinerator. Heat of combustion values of these various incineration substances are used in energy balances, and ultimate analysis are used in material balances.

Heat of combustion values of solid waste samples are normally determined experimentally (Parr, 1966; D. L. Wilson, 1971, unpublished data). However, some materials, especially incinerator ashes, are

difficult to analyze. Futhermore, because the experimental data is not compared to other thermal analyses, the accuracy of the heat of combustion values is questionable.

Solid waste materials are complex entities and very heterogeneous, therefore, data obtained with methods which analyze solid wastes samples for specific components cannot be interpreted independently. Likewise, for both the scientist and engineer to have a real understanding of solid wastes materials, all analytical data, achieved upon testing the substances, should be correlated into a complete concept. The scientist and engineer must coordinate their tasks so that each method of analysis is so designed that the data is meaningful to all parties and can be correctly applied to a solid waste problem.

This paper is an attempt to correlate data from different analyses into a formula for the heat of combustion determination of solid wastes samples. This correlation of methods adds more understanding to each analytical method and to the application of its data.

APPROACH AND RESULTS

The usual formula (McGraw-Hill, 1967a), established about 1818, for determining heat of combustion of coal from an ultimate analysis is that of Dulong:

$$1. \quad \text{Btu/\#} = 14{,}544C + 62{,}028\left(H - \frac{O}{8}\right) + 4050S$$

Where C, H, O, and S are the decimal percents of carbon, hydrogen, oxygen, and sulfur found on ultimate analysis. In this paper, each

component of this Dulong formula will be discussed independently and some new terms will be added, thus creating a modified formula recommended for solid wastes samples.

By definition (Schmidt and List, 1962a), complete combustion of a fuel involves the conversion of all carbon to CO_2, hydrogen to H_2O, and sulfur to SO_2. The numbers 14544, 62028, and 4050 in the Dulong formula represent the heat of formation of one mole of CO_2 from graphite carbon, the heat of formation of one-half mole of water from hydrogen and oxygen gases, and the heat of formation of one mole of SO_2 from sulfur, respectively. The term $(H - \frac{O}{8})$ represents the available hydrogen (Schmidt and List, 1962a).

Since the Dulong formula was established about 1818, using recent heat of formation values (McGraw-Hill, 1967b) the Dulong formula is updated to the following formula:

$$2. \quad Btu/\# = 14{,}096C + 61{,}054\ (H - \frac{O}{8}) + 3982S$$

Since the calculated Btu/# values are to be compared with experimental Btu/# values obtained in a constant volume calorimeter (Parr, 1966; D. L. Wilson, 1971, unpublished data), the heat of formation of water becomes 60,214 Btu/# (Schmidt and List, 1962b). The updated constant volume formula is:

$$3. \quad Btu/\# = \underbrace{14{,}096C}_{\textit{SECTION I}} + \underbrace{60{,}214\ (H - \frac{O}{8})}_{\textit{SECTION II}} + \underbrace{3982S}_{\textit{SECTION III}}$$

For clarification, the formula will be discussed in sections.

SECTION I: The value 14096 Btu/# is the heat of reaction for the following:

4. $C_{(graphite)} + O_{2(gas)} \rightarrow CO_{2(gas)}$

This value does not account for carbonate carbon content of solid waste samples. The "C" in this section should represent the decimal percent of organically-bonded carbon content, determined experimentally (D. L. Wilson, Environ. Sci. Technol., in press). Another section, *SECTION IV*, must be added to the Dulong formula to account for the carbonate carbon content, determined experimentally (AOAC, 1970a; D. L. Wilson, 1971, unpublished data).

SECTION IV: All carbonates in solid wastes samples are assumed to be calcium carbonate. The heat of decomposition of one mole of calcium carbonate is 6382 Btu/# (McGraw-Hill, 1967c). This value is multiplied by the decimal percent of carbonate carbon content found in the sample. Since decomposition of calcium carbonate is endothermic and the formula is the sum of exothermic values, the total value of *SECTION IV* must be preceded by a minus sign.

The Dulong formula becomes the following:

$$\text{5. Btu/\#} = \underbrace{14{,}096\, C_{(organic)}}_{\textit{SECTION I}} + \underbrace{60{,}214\, (H - \tfrac{O}{8})}_{\textit{SECTION II}} + \underbrace{3982S}_{\textit{SECTION III}} - \underbrace{6382\, C_{(inorganic)}}_{\textit{SECTION IV}}$$

SECTION II: The value 60214 Btu/# is the heat of reaction for the following (at constant volume):

6. $1/2\, H_{2(g)} + 1/4\, O_{2(g)} \rightarrow 1/2\, H_2O_{(\ell)}$

The 60214 value is for one-half mole of water instead of one mole because only hydrogen (as H) is involved in the formula.

The "H" in this section should represent the decimal percent of the total hydrogen content, determined experimentally (D. L. Wilson, Environ. Sci. Technol., in press). Since the carbonate oxygen is already accounted for in *SECTION IV*, the "O" in this section should represent the decimal percent of only the organically-bonded oxygen content, mathematically determined (D. L. Wilson, submitted for publication in Environ. Sci. Technol.).

SECTION V: Since the heat of reaction value, 60214, is for formula 6, the Dulong formula does not consider that the hydrogen and oxygen contents of the sample are not gases but are bonded to other elements. Another section, *SECTION V*, must be added to the formula to include the energy envolved in the formation of the hydrogen gas. Assuming all the hydrogen is bonded to carbon and employing certain bond energy values (Glasstone, 1960), the energy released in the formation of hydrogen gas is 8929 Btu/#. Since hydrogen in the formula is as "H" and not "H_2" the available hydrogen concentration is divided by two before multiplying by 8929.

SECTION VI: The energy released in the formation of oxygen gas is determined similar to the above for hydrogen gas and found to be 4274 Btu/#. *SECTION VI* accounts for the energy released in the formation of oxygen gas by dividing decimal percent of organically-bonded oxygen by two and then multiplying this value by 4274.

The formula now becomes as follows:

$$7.\quad \text{Btu/\#} = \underbrace{14{,}096\ C_{(\text{organic})}}_{\textit{SECTION I}} + \underbrace{60{,}214\ (H - \tfrac{O}{8})}_{\textit{SECTION II}} + \underbrace{3982\ S}_{\textit{SECTION III}} - \underbrace{6382\ C_{(\text{inorganic})}}_{\textit{SECTION IV}} + \underbrace{8929\ (\tfrac{H - \frac{O}{8}}{2})}_{\textit{SECTION V}} + \underbrace{4274\ (\tfrac{O}{2})}_{\textit{SECTION VI}}$$

SECTION III: The value 3982 Btu/# is the heat of the reaction for the following:

$$8.\quad S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)}$$

The concentration of sulfur in solid waste samples is generally consistant (D. L. Wilson, submitted for publication in Environ. Sci. Technol.) and, in this paper, is considered to be 0.20%, unless actually determined (ASTM, 1969).

SECTION VII: The term "heat of combustion" generally includes not only carbon, hydrogen, oxygen, and sulfur but also other elements such as nitrogen and chlorine which may be present in the sample (Parr, 1966). Since nitrogen is usually present in solid waste samples, *SECTION VII* is added to the formula to compensate for the oxidation of nitrogen to nitrogen dioxide. Again using handbook heat of formation values (McGraw-Hill, 1967c) the heat of oxidation of the nitrogen is 1040 Btu/#. Nitrogen content of solid waste materials is consistant but varies with the nature of the material (D. L. Wilson, submitted for publication in Environ. Sci. Technol.). In this paper, nitrogen concentration, unless actually determined (AOAC, 1970b; N. S. Ulmer and W. H. Kaylor, submitted for publication in Environ. Sci. Technol.)

is assumed to be 0.75% for raw refuse samples and 0.15% for incinerator residue samples and fly ash samples. For the formula, "N" represents the decimal percent of nitrogen content in the sample and is multiplied by 1040. This product accounts for the heat generated during the oxidation of nitrogen to nitrogen dioxide.

Chlorine, although present in solid waste samples and its concentration enters in the calculations for oxygen content (D. L. Wilson, submitted for publication in Environ. Sci. Technol.), is not considered a factor in the heat of combustion calculations. Assuming the chlorine to be present as sodium chloride, the sodium chloride is postulated to react with water to form sodium hydroxide which then reacts with sulfuric acid present to form sodium sulfate (Barker, Mott, and Thomas, 1955). Considering the general concentrations of chlorine and sulfur in coal, these two reactions product a net thermochemical effect which is almost nil. If the occasion arises that solid wastes samples contain excessive amounts of chlorine, as apposed to sulfur content, then the chlorine concentration may be incorporated into the formula.

The final modified Dulong formula for solid wastes samples is as follows:

$$9.\quad \text{Btu/\#} = \underbrace{14{,}096\ C_{(\text{organic})}}_{\text{SECTION I}} + \underbrace{60{,}214\ \left(H - \frac{O}{8}\right)}_{\text{SECTION II}} + \underbrace{3982\ S}_{\text{SECTION III}} - \underbrace{6382\ C_{(\text{inorganic})}}_{\text{SECTION IV}} + \underbrace{8929\ \left(\frac{H - \frac{O}{8}}{2}\right)}_{\text{SECTION V}} + \underbrace{4274\ \left(\frac{O}{2}\right)}_{\text{SECTION VI}} + \underbrace{1040\ N}_{\text{SECTION VII}}$$

For ease of calculation, the formula is arranged as such:

$$10.\quad \text{Btu/\#} = 14{,}096\ C_{(org.)} + 60{,}214\ (H - \frac{O}{8}) + 1040\ N + 3982\ S + 8929\ (\frac{H - \frac{O}{8}}{2}) + 4274\ (\frac{O}{2}) - 6382\ C_{(inorg.)}$$

This final modified Dulong formula has been applied to some prepared solid waste samples (Cohen and Allen, 1970) from various incinerators (Table 1). The Btu/# contents of these same samples have also been determined experimentally (Parr, 1966; D. L. Wilson, 1971, unpublished data). The Btu/# variation between experimental values and calculated values has about the same magnitude as variation between replicate Btu/# experimental values.

CONCLUSIONS

The Dulong formula for calculating Btu/# of coal samples has been modified until it can successfully be applied to solid wastes samples.

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The author thanks the Division of Technical Operations, Solid Waste Management Office, for the provision of samples from incinerators.

Mr. Israel Cohen, Solid Waste Management Office, prepared many of the samples used for comparison with the formula.

Personnel at the Research Services Laboratory, Solid Waste Management Office, performed most of the laboratory analyses mentioned in this paper.

Personnel at the Louisville Testing Laboratory, Inc., Louisville, Kentucky, under contract with Solid Waste Management Office, provided the nitrogen and sulfur data mentioned and the chlorine data referred to in this paper.

TABLE 1

COMPOSITION AND HEATING VALUE OF PREPARED SOLID WASTES INCINERATOR SAMPLES[a]

Sample No.	Type of Sample	Ultimate Analysis						Exp. Btu/#	Exp. Variation	Calc. Btu/#
		% $C_{org.}$	% $C_{inorg.}$	% H	% $O_{org.}$	% N	% S			
434	Raw Refuse	45.68	0.25	6.28	35.34	0.54	0.24	8425	50	8397
435	"	46.76	0.42	6.23	39.82	0.44	0.22	8336	109	8238
436	"	46.51	0.65	6.38	37.92	0.60	0.14	8442	46	8397
437	"	46.25	0.50	6.35	38.05	0.67	0.10	8377	50	8340
442	"	45.61	0.31	6.42	30.18	1.10	0.18	8688	202	8786
443	"	44.25	0.47	5.96	37.82	0.53	0.30	8087	83	7829
444	"	46.17	0.72	6.52	37.67	0.56	0.14	8452	63	8449
445	"	46.85	0.83	6.61	35.94	1.03	0.10	8707	21	8705
5	"	46.70	0.09	6.40	31.88	0.75*	0.20†	8594	184	8839
7	"	43.55	0.72	6.25	33.87	0.75*	0.20†	8192	197	8139
8	"	45.74	0.59	6.02	35.54	0.75*	0.20†	8199	57	8207
9	"	43.49	0.31	5.74	33.64	0.68	0.12	7846	224	7837
99	"	43.77	0.10	6.35	35.47	0.75*	0.20†	7904	178	8179
100	"	43.79	0.14	6.22	36.86	0.75*	0.20†	8055	18	8008
101	"	42.84	0.16	6.12	35.02	0.93	0.34	7624	32	7926
102	"	44.74	0.16	6.36	31.01	0.81	0.34	8209	68	8585
103	"	45.91	0.10	6.38	37.05	0.93	0.31	8222	36	8411
165	"	45.16	0.03	6.35	39.12	0.72	0.17	7967	9	8158
166	"	44.35	0.09	6.19	34.57	0.72	0.17	8267	36	8209
167	"	44.43	0.08	6.32	38.69	0.62	0.11	8174	14	8052
168	"	45.58	0.08	6.57	39.85	1.42	0.11	7988	4	8319
169	"	52.35	0.04	6.96	33.60	1.42	0.11	10204	156	9899
438	Res. (Fines)[b]	6.87	0.15	0.17	0.00	0.12	0.21	1192	142	1079
439	"	3.65	0.07	0.08	0.00	0.04	0.12	609	42	567
440	"	4.61	0.05	0.07	0.00	0.04	0.18	805	35	700
446	"	13.69	0.17	0.11	0.00	0.11	0.27	2245	108	2002
447	"	6.06	0.16	0.12	0.00	0.12	0.21	1003	54	931
448	"	9.46	0.42	0.14	0.00	0.16	0.24	1575	56	1408

TABLE 1 (Con't.)

COMPOSITION AND HEATING VALUE OF PREPARED SOLID WASTES INCINERATOR SAMPLES[a]

Sample No.	Type of Sample	Ultimate Analysis						Exp. Btu/#	Exp. Variation	Calc. Btu/#
		% $C_{org.}$	% $C_{inorg.}$	% H	% $O_{org.}$	% N	% S			
10	Res. (Fines)[b]	1.40	0.65	0.18	0.00	0.15*	0.20†	226	74	282
13	"	0.66	0.58	0.16	0.54	0.15*	0.20†	154	116	135
15	"	0.72	0.42	0.10	0.00	0.15*	0.20†	167	95	149
17	"	0.72	0.51	0.11	0.06	0.13	0.13	114	125	141
104	"	10.55	0.56	0.70	2.45	0.36	0.43	1549	130	1778
106	"	7.57	0.76	0.54	3.18	0.28	0.41	1035	2	1196
108	"	8.52	0.52	0.55	1.85	0.22	0.68	1143	186	1444
110	"	7.22	0.70	0.42	2.94	0.15*	0.20†	959	168	1078
112	"	17.25	0.93	0.90	5.34	0.15*	0.20†	2493	10	2645
171	"	2.14	0.40	0.20	0.00	0.31	0.37	357	16	423
173	"	1.19	0.15	0.06	0.00	0.23	0.24	254	10	209
11	Res. (Org.)	15.81	0.64	2.24	11.04	0.75*	0.20†	3394	580	2996
16	"	8.08	2.59	1.04	3.76	0.75*	0.20†	1729	183	1439
18	"	11.23	1.24	1.48	8.61	0.75*	0.20†	2126	193	1962
105	"	29.54	0.44	3.39	15.73	0.75*	0.20†	4588	126	5399
107	"	33.56	0.40	4.41	15.65	0.75*	0.20†	6535	18	6639
109	"	33.40	0.18	4.06	24.47	0.75*	0.20†	5525	190	5882
111	"	28.16	0.50	3.93	14.30	0.75*	0.20†	5584	2	5643
113	"	33.67	0.50	3.93	20.55	0.75*	0.20†	5940	106	6049
170	"	33.86	0.14	4.74	27.01	0.75*	0.20†	6020	130	6236
172	"	50.45	0.14	4.68	27.88	0.75*	0.20†	8539	20	8490
19	Fly Ash	3.48	0.94	0.13	0.00	0.15*	0.20†	565	75	524
20	"	2.51	1.08	0.16	0.00	0.15*	0.20†	456	53	398
21	"	3.15	1.16	0.11	0.00	0.15*	0.20†	601	73	451
22	"	2.16	1.23	0.13	0.00	0.15*	0.20†	422	65	319
23	"	2.15	1.31	0.17	0.00	0.15*	0.20†	278	57	338
24	"	2.04	0.96	0.09	0.79	0.15*	0.20†	335	85	253

TABLE 1 (Con't.)

COMPOSITION AND HEATING VALUE OF PREPARED SOLID WASTES INCINERATOR SAMPLES[a]

Sample No.	Type of Sample	Ultimate Analysis						Exp. Btu/#	Exp. Variation	Calc. Btu/#
		% $C_{org.}$	% $C_{inorg.}$	% H	% $O_{org.}$	% N	% S			
91	Fly Ash	4.14	0.08	0.22	0.10	0.15*	0.20†	581	46	723
92	"	3.36	0.15	0.22	0.25	0.15*	0.20†	483	144	602
93	"	2.84	0.12	0.20	0.12	0.15*	0.20†	367	80	521
94	"	1.27	0.11	0.13	0.00	0.10	0.59	195	38	280
96	"	1.04	0.35	0.16	0.23	0.15*	0.20†	188	84	223
97	"	3.45	0.15	0.24	0.57	0.15*	0.20†	543	26	608

* Nitrogen value is estimated.

† Sulfur value is estimated.

[a] All values are on a dry basis. Each value is the average of at least two individual analysis. A total of sixty-one samples are from five incinerators located throughout the United States.

[b] Residue "Fines" or "Noncombustibles" are materials remaining after most of the readily combustible substances have been removed by manual sorting. The sorting was performed at the incinerator cite and a 1/2-inch sieve was employed to assist in the separation.

[c] Residue "Organics" or "Combustibles" are mostly the readily combustible materials. Unlike "Fines" these materials are usually retained on a 1/2-inch sieve.

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